Thermally induced structural changes In Twaron Fibres using crystallographic data

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ABSTRACT

The high strength, high modulus Twaron fibers are made up ofpoly (p-phenylene terephthalamide) or PPTA. Since these fibres are recommended for high temperature applications, it is essential to study the thermal properties ofthese fibres to have the optimum utilization in practice. This paper presents the X-ray analysis on the effect of in situ heating on the crystallographic unit cell dimensions of twaron. Variations of basal plane and axial dimension have been studied with temperature. These dimensional changes have been used to estimate the corresponding coefficient of thermal expansion along the basal plane (α_A) and axial direction (α_C). Enlargement of the unit cell with the thermal heating is a common behavior but the Twaron fibers behave differently. There is a thermal expansion along basal plane and contraction along the axial dimension. The axial contraction has been correlated to partial changes in molecular conformation and molecular dimensions. In contrast to axial dimension, there is thermal expansion along the basal plane. Expansion is more along a-direction than b-direction, which again is related to crystal structure of Twaron. Along a-direction, adjacent layers stack together via week Van der Watt's interactions. So deformation in any form say thermal or otherwise is expected to influence the week interactions. However, in b-direction, adjacent chains are linked by hydrogen bonds. Variation ofvolume has also been studied with temperature and it is found to increase with temperature. So, although there is contraction along c-direction and expansion along basal plane, overall there is expansion in the unit cell volume.

1.Introduction

Aramid fibres made of poly (p-phenylene terephathalamide, PPTA) (1) are characterized by lightweight, high strength, high modulus with good thermal stability, high impact resistance and vibration damping properties. Because of these unique features aramid fibres find applications in high performance composites (2).

The measurement of the properties of these fibres is an important step in their optimum utilization in practice. Since the composites based on polymer matrix with fibre reinforcement are cured at elevated temperatures, a mismatch of thermal expansion between the matrix and fibre introduces undesirable thermal stresses. So it is important to study the effect of insitu heating on crystallographic properties of fibres.

Unlike conventional materials, which expand on heating, some of the fibres show highly anisotropic behavior with negative coefficient of thermal expansion (CTE) along the fibre direction (axial, α_c) and a positive areal CTE (α_A) in the plane perpendicular to fibre direction. The fibres of PBO, a rigid rod isotropic polymer, exhibits negative CTE. Polyethylene with negative α_c (3) and carbon fibres with α_c (4) are some examples of industrially important fibres that show negative CTE in the axial direction. Aramid fibres also show this trend. Based on thermomechanical analyzer measurements, Rojstaczer et al. (5) have reported α_c -5.7×10^{-6} and α_A = 66.3 $\times 10^{-6}$ for Kevlar fibres, a commercially available product of DuPont, USA. The value reported by DuPont for Kevlar fibre is α_c 2×10^{-6}/°C.

The aramid fibres Twaron and Kevlar are commercially available PPTA fibres (6). These fibres contain monoclinic crystalline form of PPTA with c-axis preferentially oriented along the fibre axis. The mechanical and other properties of the fibre depend strongly on the degree of crystallinity and orientation of the crystallite in the fibre. The tensile strength and modulus of Twaron fibres are 2.92 and 64,3 GPa, respectively as compared to the corresponding values of 3.01 and 92,6 GPa for Kevlar 49 fibres (7). Because of these differences in the tensile strength and modulus values, the effect of insitu heating has been studied on Twaron fibres also.

This paper reports the variation in unit cell parameters with insitu heating of twaron fibres using X-ray diffraction technique and compares it with that of Kevlar.

2, Experimental details

Twaron fibres used in the present study were provided by Akzo Nobel, The Netherlands. X-ray diffraction data were collected using high temperature attachment for fibres for the D/MAX 2200 Ultima X-ray powder diffractometer (M/s. Rigaku International Corporation, Japan). CuKα radiation was used and a scientillation detector was employed to measure the intensity of diffracted beam. A collimator of 1mm diameter was used to collimate the X ray beam. The presence of heater assembly necessitated the 20 scan with θ_{fixed} 5" geometry. A chromel-alumel thermocouple placed close to the sample was used to measure the temperature. A bunch of Twaron fibres were held taut in the sample holder. The two intense equatorial reflections (200) and (110) were recorded by placing the fibres perpendicular to the plane of 20 scan. For recording meridional reflections, (002), (004) and (006), the sample was rotated by 90" about the beam direction using the in-

built control. In the equatorial diffraction pattern, the two most intense reflections are (200) and (110) occurring at 26 - 22,9 and 20.6°, respectively. The indexing was consistent with a monoclinic unit cell of dimensions a=7.89, b=5.18 and c=12.9 A (chain axis) and y = 90° (8). The patterns were recorded at room temperature (RT1 ≈ 20°C), 50, 100, 150, 200, 250 and 280°C. These temperatures are below the service temperature (300°C) of Twaron. At each of the chosen temperatures, heating was carried out at an approximate rate of 5°C / minute. After reaching the desired temperature, ten minutes were allowed for the temperature to stabilize. During the recording of the diffraction patterns the temperature was found to remain stable within ± 0.5°C.

3. Results and discussion

3.1 Unitcell parameters in plane perpendicular tofibre direction

Figure 1 shows the X-ray diffraction patterns from Twaron fibres recorded at different temperatures. The overlapping peaks (200) and (110) observed in the diffraction patterns were separated using peak separation software supplied by M/s. Rigaku. The profile characteristics were derived by least squares fit of a Pseudo Voigt function. The shifts in 20 values on heating can be clearly seen from these profiles.

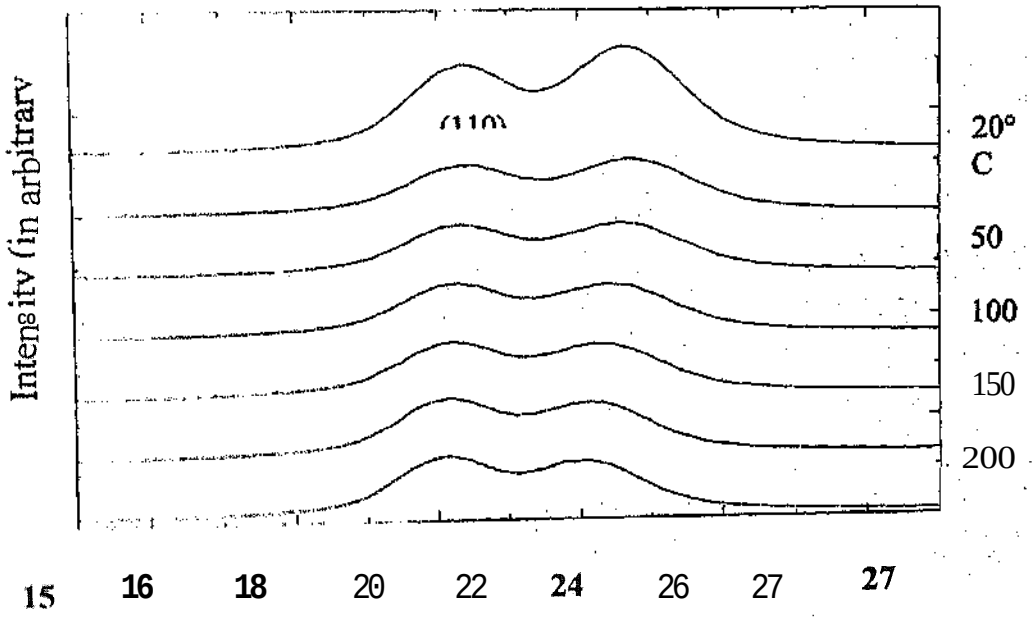

Figure 1: X-ray diffractionprofiles at various temperatures.

From the 2θ values of (200) and (110) reflections, a- and b- dimensions were calculated. Figure 2(a) and (b) presents the variation in unit cell dimension in a- and b- direction.

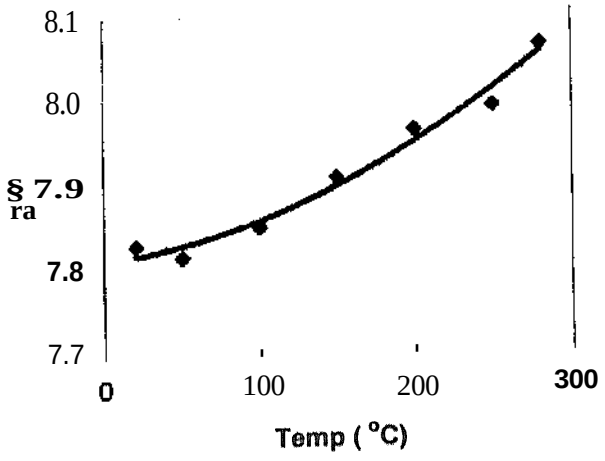

Figure 2. variation in unit cell dimension in (i) a- and (ii) b- direction

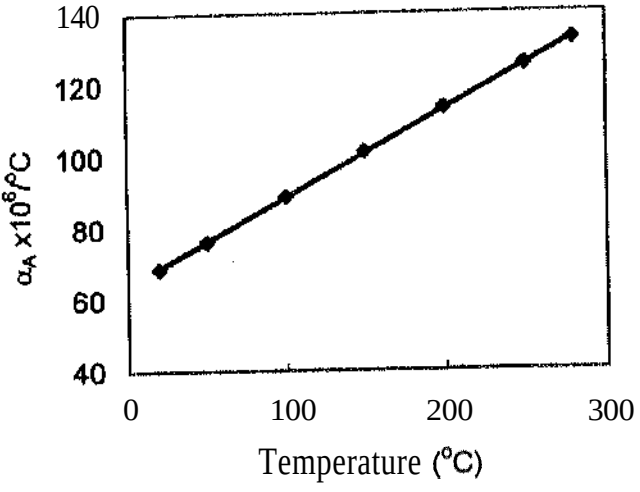

Figure 3: Variation of α_A with temperature.

The results (Figure 3) suggest that unit cell dimension a- increases with temperature. The b-values showed a linear dependence on temperature. It is seen that temperature dependence of b is much smaller than a. The variation in area A in the plane perpendicular to the fibre direction was also computed and is plotted in Figure 3.

3.2 Variation in unit cell parameter in longitudinal direction c :

Higher order reflection (006), being more sensitive, was used to study the structural changes in the c-dimension. Figure 4 presents the variation of c with tempareture. Unlike the varation of a and b, the variation in c is negative and reduces further with increase in temperature.

It may be noted that three unit cell parameters have been determined using only three reflections. This is an intrinsic limitation of the fibre pattern and imposes a limitation on the precision of the unit cell parameters.

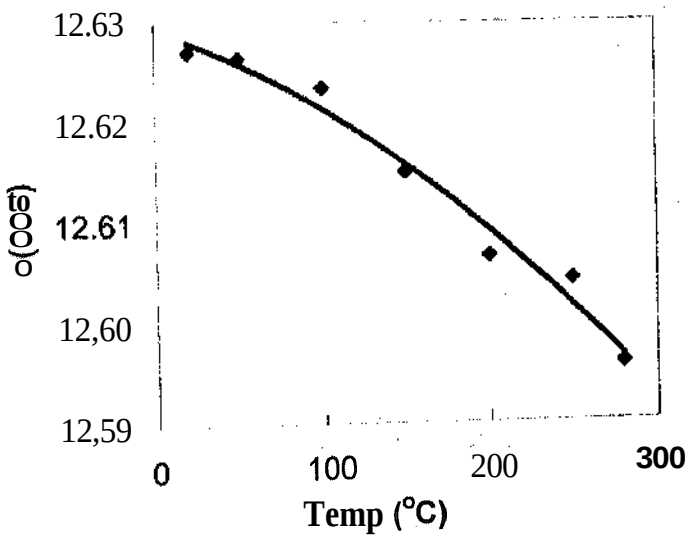

Figure 5 : variation of c with tempareture

The relative values of a and c can be explained on the basis of crystal structure of PPTA (8). The molecules oriented in the crystallographic c-direction are fully extended and assume all trans conformation. Adjacent molecules along the crystallographic b-direction interact by inter chain hydrogen bonds. The molecular arrangement along bc-plane therefore forms a layer like structure. These layers interact with each other by van der Waal's forces along the crystallographic a-direction. The higher sensitivity of the a - dimension can therefore be correlated with

the weak van der Waal's forces. The smaller variation of b with temperature results from a network of hydrogen bonds between the adjacent chains. The molecules in the c- direction, being fully extended and in all trans conformation are like rigid rods. Any temperature increase will inhibit the further axial expansion of PPTA. This reduction in c-value could be due to partial changes in the initial all trans conformation of the Twaron molecules. Similar conformational disorders have been suggested for Teflon (9) and for the changes in the axial dimension of Kevlar fibres (10-11). The reduction in unit cell parameter along the fibre direction is mostly seen in the fully extended all trans conformations. In the case of Polyethylene, the negative CTE is explained on the basis of rotation about the C-C single bonds. Such type of rotation about the single bonds does not exist in the case of PPTA. In the case of PPTA, the phenyl group of terephthalic segment is tilted with respect to the adjacent amide plane by 30° and the phenyl group of the p-phenylene diaminc segment is tilted with respect to the same amide plane by 35°. Free rotations about the phenyl carbonyl group and the phenyl nitrogen bonds are restricted by steric hinderances marked in figure 7. Variation in the angle of tilt due to thermal exposurc may vary the steric effects. These variations in steric effects that are responsible for a rigid rod like character to the PPTA chain can result in contraction along axial dimension.

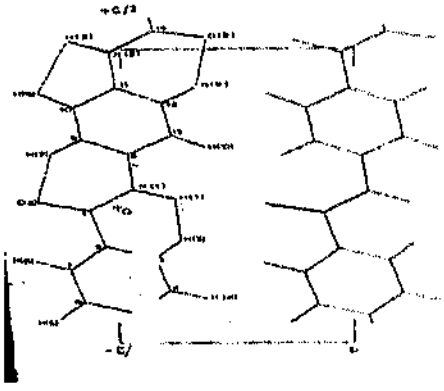

Figure 7 ; Arrangement of PPTA molecules in (100) plane. Steric interactions arc shown by dotted lines.

3.3 Unit cell volume

Although the basal area increases and c-length reduces, the overall unit cell volume increases. Fig presents the variation of unit cell volume with temperature.

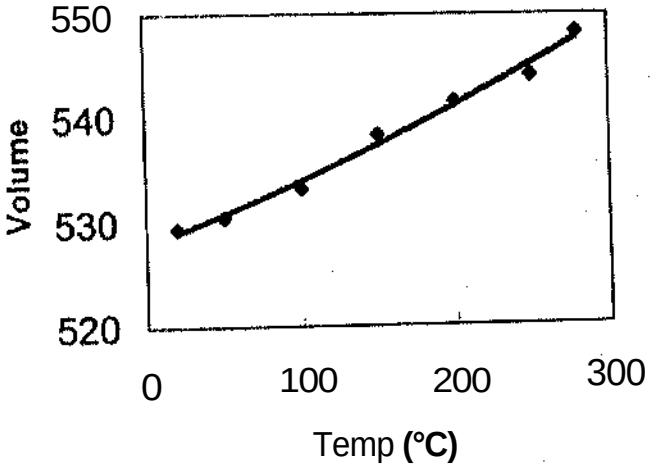

Figure 8 : Variation in unit cell volume with temperature.

4, Conclusions

The variation in unit cell parameters with insitu heating of Twaron fibres using X-ray diffraction technique are determined along the fibre direction (α_c) and areal CTE in the plane perpendicular to fibre direction. The monoclinic unit cell exhibits an anisotropic behaviour. There is thermal contraction along c-direction amd expansion along the basal plane. The behaviour of thermal expansion is compared with Kevlar fibres, which are also made up of the same polymer.

Acknowledgement

1 wish to thank Dr. R V Krishnan, Head, Materials Science Division, NAL, for his continuous support and valuable suggestions.

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